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**Relevance of intracellular partitioning of metals in prey to differential metal bioaccumulation among populations of mummichogs (*Fundulus heteroclitus*)**

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## Abstract

Intracellular partitioning of trace metals is critical to metal tolerance in aquatic organisms and may also influence metal trophic transfer in ecosystems. In this study, we tested the relevance of metal (Cd, Cu, Pb, and Zn) intracellular partitioning in prey as an indicator of metal trophic availability to benthic forage fish, mummichogs (*Fundulus heteroclitus*), in chronically metal-polluted salt marshes in New York, USA. Two common prey of mummichogs in the study area, *Palaemonetes pugio* and *Nereis acuminata*, generally stored increasingly higher proportions of non-essential metals (particularly Pb) in insoluble (less trophically available) cellular components, as the whole body burdens increased. In contrast, intracellular partitioning of essential metals (Cu and Zn) in invertebrate prey varied relatively little among sites. Differential Cd and Pb intracellular partitioning patterns within *P. pugio* among sites were significantly associated with Cd and Pb whole body burdens in mummichogs, respectively (i.e., prey-driven bioreduction of metals), while bioaccumulation of Cu and Zn in mummichogs was similar among populations. The findings in this study suggest that metal intracellular partitioning within prey may be partially responsible for metal trophic availability to a predator in metal-polluted habitats, while there was also evidence that some predator-dependent processes may offset differential trophic availabilities from prey.

**Key words:** Metals; zoobenthos; forage fish; salt marshes; metal trophic transfer; metal intracellular partitioning; *Fundulus heteroclitus*; New York, USA

## 1. Introduction

In the past decade, an increasing number of studies have explored ecological and evolutionary implications for intracellular partitioning of trace metals within aquatic organisms in chronically polluted habitats (e.g., Martin et al., 2007; Perceval et al., 2004). Chronic trace metal pollution can exert selection pressure on organisms (Klerks and Weis, 1987; Luoma, 1977), ultimately eliminating local populations of metal-sensitive species and allowing metal-tolerant species to dominate biological communities (Clements, 1997). Differential tolerance to trace metals among populations or species is often associated with intracellular metal storage within aquatic organisms (e.g., Buchwalter et al., 2007; Perceval et al., 2004). Metal-tolerant species generally possess physiological or biochemical mechanisms that allow them to cope with an elevated level of bioavailable trace metals in the environment (Mason and Jenkins, 1995). These mechanisms include sequestration to metal-binding proteins (e.g., metallothioneins) (Mason and Jenkins, 1995; Roesijadi, 1992) and formation of granular concretions (or metal-rich granules) (Klerks and Bartholomew, 1991; Mason and Jenkins, 1995).

Experimental studies have demonstrated that intracellular partitioning of trace metals in prey can also influence metal trophic availability to their predators (e.g., Cheung and Wang, 2005; Wallace and Luoma, 2003). The importance of dietary ingestion of trace metals as a predominant route for metal bioaccumulation in aquatic organisms has been well documented (e.g., Griscom et al., 2002; Wang, 2002). Trace metals accumulated in prey can be transferred to and potentially cause secondary toxic effects in their predators (Baines et al., 2002; Ni et al., 2000). Differential intracellular partitioning of trace metals among chronically metal-exposed populations or species may thus have important implications for ecological impacts that cascade through food chains in ecosystems.

The relevance of intracellular metal distributions within prey to metal trophic transfer results from differential trophic availabilities of metals distributed among various cellular components (Wallace and Lopez, 1997; Zhang and Wang, 2006). As trace metals bound to organelles and cytosolic proteins (including metal-binding proteins) are readily solubilized by the digestive processes of a predator, metals associated with these cellular components are thought to be more available to a predator than those with other components (Wallace and Lopez, 1997; Zhang and Wang, 2006). Due to their high bioavailabilities to predators, Wallace and Luoma (2003) have suggested that metals associated with cytosolic proteins and organelles within prey be compartmentalized as ‘trophically available metal’ (TAM). In contrast, trace metals partitioned to insoluble components such as metal-rich granules within prey are not readily available to many predators, as most granules are not easily solubilized by the digestive processes (Nott and Nicolaidou, 1994; Wallace and Lopez, 1997). The majority of trace metals sequestered into granules within prey can pass through the digestive tract of a predator without being assimilated (Rainbow et al., 2004; Wallace and Lopez, 1997). Determining intracellular partitioning of trace metals within prey may, therefore, be used to 1) understand specific metal trophic pathways and 2) estimate the extent of potential metal trophic transfer efficiency when assessing ecological impacts associated with trace metal pollution.

In the present study, we tested the relevance of metal intracellular partitioning in prey as an indicator of differential metal trophic availability to mummichogs, *Fundulus heteroclitus* (Pisces: Cyprinodontidae), in metal-polluted tidal salt marshes in New York, USA. Mummichogs are among the most abundant fishes in tidal creeks and salt marshes in the northwest Atlantic coast (Nixon and Oviatt, 1973). Like many benthic predators, mummichogs primarily feed on a variety of benthic macroinvertebrates (Kneib et al., 1980), which are in direct contact with sediments

(the main source of trace metals in benthic food chains). Elevated levels of sediment-associated trace metals have persistent and cumulative effects, inducing various ecological and physiological alterations in marine organisms living in urban coastal habitats (Luoma, 1996). Furthermore, mummichogs play an essential role as an intermediate predator linking sediment-associated invertebrates to piscivorous fishes and wading birds using tidal salt marshes and inland wetlands as feeding grounds (Kneib and Wagner, 1994). Understanding factors determining the extent of metal trophic availability to mummichogs (a conduit of trace metal transfer to top predators) would, therefore, provide much needed information on potential ecological impacts of trace metal pollution in urban coastal ecosystems.

## **2. Materials and methods**

### *2.1. Study area*

This study was conducted in the Arthur Kill–AK (part of the New York/New Jersey–NY/NJ Harbor Estuary Complex), which is a tidal waterway located between northern NJ and Staten Island, NY, connecting Newark Bay and Kill van Kull to the north, and Raritan Bay, NY Harbor, and the Atlantic Ocean to the south (Fig. 1). Due to chronic pollution (e.g., chemical discharges from industrial facilities and sewage treatment plants), the water quality of the NY/NJ Harbor Estuary has been severely degraded for more than a century (Crawford et al., 1994). The highest levels of some chemical pollutants occur in tributaries of AK (Weis et al., 2001). Since tides enter from both ends of AK (Fig. 1), this region is poorly flushed, resulting in enhanced entrapment and accumulation of pollutants in sediments (Bopp et al., 2006).

Specific study sites were four tributaries of AK; Richmond Creek, Main Creek, Neck Creek, and Mill Creek and two regional reference sites external to AK; Lemon Creek and Great Kills

Harbor (Fig. 1 and Table 1). Neck Creek is polluted with various chemicals due to its proximity to many oil refineries as well as abandoned industrial facilities (Ward, 2002). Richmond Creek and Main Creek are tributaries of Fresh Kills Complex and are surrounded by the Landfill. Mill Creek is located near the confluence of AK and Raritan Bay and has been polluted from historic smelting activities in the area. Lemon Creek is one of a few relatively undisturbed tidal salt marshes in the region. Despite its proximity to sewage treatment plants, Great Kills Harbor, which is located on the eastern shore of Staten Island, has relatively low levels of most pollutants.

## 2.2. Samplings of mummichogs and benthic macroinvertebrate prey

Samplings of mummichogs and two of the most commonly consumed prey items of mummichogs in AK, decapods (*Palaemonetes pugio*) and polychaetes (*Nereis acuminata*) (Goto, 2009), were conducted during the summers (June to September) of 2001 and 2004. Large adult mummichogs (> 70 mm TL) were collected using a seine net with polyester mesh or cylindrical minnow trap. *N. acuminata* was collected by sieving bulk sediments through a 500 µm-mesh sieve, while adult *P. pugio* (> ~25 mm TL) was collected using a D-frame dip net. Mummichogs, *P. pugio*, and *N. acuminata* were then transported on ice to laboratory.

## 2.3. Laboratory sample processing of mummichogs and benthic macroinvertebrate prey

In the laboratory, mummichogs and macroinvertebrates were allowed to depurate gut contents for at least 24 hours in filtered 15‰ seawater. Mummichogs were then immediately euthanized by an overdose of MS222. Macroinvertebrates and mummichogs were then stored in a freezer (−80 °C) for subsequent fractionation and/or metal analyses (Sections 2.4 and 2.5).



#### 2.4. Isolation of TAM from benthic macroinvertebrate prey

Trace metals associated with the trophically available metal (TAM) compartment were isolated from *P. pugio* and *N. acuminata* using a centrifugation technique (Wallace and Luoma, 2003). Macroinvertebrates ( $n = 5$  per site for prey species; each sample = ~500 mg of tissues) were thawed on ice, dabbed dry, and weighed. Tissues were then transferred into pre-weighed centrifuge tubes and homogenized (under a nitrogen atmosphere) in cold TRIS buffer (20 mM, pH = 7.6) with a Polytron tissue homogenizer (Kinematica, Luzern, Switzerland) (Wallace and Luoma, 2003). The homogenates were fractionated by centrifugation at 1,450 x g for 15 minutes, which produced a pellet containing tissue fragments and cellular debris, and a supernatant containing cytosolic proteins and organelles (i.e., TAM) (Wallace and Luoma, 2003). Each fraction was processed for metal analyses, as described below (Section 2.5).

#### 2.5. Analyses of metals in mummichogs and benthic macroinvertebrate prey

Resultant supernatants and pellets from fractionated macroinvertebrates as well as a whole body of mummichogs were oven-dried (~70 °C) for 24 to 48 hours and weighed (dry weight). Samples were then digested under reflux with concentrated Trace Metal Grade nitric acid (5 ml) overnight at room temperature (~20 °C) and subsequently on a hotplate (~80 °C) for ~48 to 72 hours. Once digested, samples were evaporated to dryness, re-suspended in 2% nitric acid (8 ml), and filtered (0.45 µm). Metal concentrations in samples were analyzed with graphite furnace atomic absorption spectrometer for cadmium (Cd), copper (Cu), and lead (Pb), or flame atomic absorption spectrophotometer for zinc (Zn) (Perkin Elmer 3100AAS with AS-60).

As quality assurance, Standard Reference Material<sup>®</sup> (mussel tissue, SRM 2976, National Institute of Standards and Technology, USA) was processed and analyzed for Cd, Cu, Pb, and Zn, as described above. The average recovery rates of Cd, Cu, Pb, and Zn were 95.3, 100.3, 63.5, and 96.3%, respectively. Procedural and reagent blanks were also analyzed for potential secondary metal contamination. Select calibration standard solutions of each metal were analyzed every 10 samples. When the deviation from the initial values was more than  $\pm 10\%$ , the instrument was recalibrated. The correlation coefficients of calibration curves were maintained  $> 0.999$  for the analysis. All standard solutions and samples were prepared with NANOpure<sup>®</sup> (reagent-grade) water. All glassware was soaked in 10% hydrochloric acid overnight, rinsed once with deionized water, and rinsed twice with NANOpure<sup>®</sup> water.

## 2.6. Statistical analyses

The normality of data was tested using Shapiro-Wilk's  $W$  test. The homogeneity of variance was tested using Levene's test. Proportional data were arcsine-transformed, and concentration data were  $\log_{10}$ -transformed before analyses, when necessary. The statistical significance of differences in whole body burdens of mummichogs among populations was tested using one-way analysis of variance (ANOVA), which, if significant, was followed by Tukey's honestly significant difference (HSD) test. Relationships between trace metals associated with TAM and whole body burdens in *P. pugio* and *N. acuminata* were analyzed with linear and nonlinear regressions, which were fitted by the Levenberg-Marquardt least squares algorithm. As all variables were subject to measurement error, relationships between trace metals associated with TAM in *P. pugio* or *N. acuminata* and whole body burdens in mummichogs were analyzed with

reduced major axis (RMA) or model II regression (Sokal and Rohlf, 1995). All statistical analyses were performed using Statistica 7.1 (Statsoft, Inc<sup>®</sup>, USA).

### 3. Results

#### 3.1. Intracellular partitioning of trace metals to TAM in prey

The concentration of Cd partitioned to the trophically available metal (TAM) compartment (TAM-[Cd]) was significantly correlated with Cd whole body burden (WB-[Cd]) in *Palaemonetes pugio* in both 2001 and 2004 (Fig. 2a and 2b, respectively). Although there was a significant correlation between the proportion of Cd associated with TAM (TAM-Cd%) and WB-[Cd] in *P. pugio* in 2001, TAM-Cd% in *P. pugio* was approximately 40% of WB-[Cd] at all sites (Fig. 2c). In 2004, there was no relationship between TAM-Cd% (~60%) and WB-[Cd] in *P. pugio* (Fig. 2d).

In *Nereis acuminata*, there was a significant correlation between TAM-[Cd] and WB-[Cd] in both 2001 and 2004 (Fig. 2e and 2f, respectively) with a disproportionately low TAM-[Cd] at Main Creek ( $0.30 \mu\text{g}\cdot\text{g}^{-1}$ ) in 2001 (Fig. 2e). TAM-Cd% in *N. acuminata* varied from 26.9% at Main Creek to 74.8% at Great Kills Harbor and was negatively correlated with WB-[Cd] in 2001 (Fig. 2g). In 2004, however, there was no relationship between TAM-Cd% and WB-[Cd] in *N. acuminata* (Fig. 2h).

The concentration of Pb in TAM (TAM-[Pb]) in *P. pugio* was significantly correlated with the Pb whole body burden (WB-[Pb]) in both 2001 and 2004 (Fig. 3a and 3b, respectively). The proportion of Pb in TAM (TAM-Pb%) in *P. pugio* was negatively correlated with WB-[Pb] in both 2001 and 2004 (Fig. 3c and 3d, respectively). In 2001, TAM-Pb% in *P. pugio* varied from ~25% at Neck Creek and Richmond Creek to 63.9% at Great Kills Harbor (Fig. 3c), while in

2004, TAM-Pb% in *P. pugio* varied from 34.8% at Mill Creek to ~52% at Lemon Creek, Richmond Creek, and Great Kills Harbor (Fig. 3d).

In *N. acuminata*, both TAM-[Pb] and TAM-Pb% were significantly correlated with WB-[Pb] in 2001 (Fig. 3e and 3g, respectively). Despite its high WB-[Pb], TAM-[Pb] and TAM-Pb% in *N. acuminata* at Main Creek were disproportionately lower than those at the other sites. In 2004, both TAM-[Pb] and TAM-Pb% were also significantly correlated with WB-[Pb] (Fig. 3f and 3h, respectively) but varied relatively little among sites.

Significant correlations were observed between the concentration of Cu in TAM (TAM-[Cu]) and the Cu whole body burden (WB-[Cu]) in *P. pugio* in both 2001 and 2004 (Fig. 4a and 4b, respectively). The proportion of Cu associated with TAM (TAM-Cu%) in *P. pugio* remained relatively constant (~80%) across the sites in 2001, with the exception of Mill Creek (~60%), resulting in no relationship with WB-[Cu] (Fig. 4c). Similarly, in 2004, although TAM-Cu% was significantly correlated with WB-[Cu] in *P. pugio*, it generally remained ~80% at all sites (Fig. 4d).

In *N. acuminata*, TAM-[Cu] was significantly correlated with WB-[Cu] in both 2001 and 2004 (Fig. 4e and 4f, respectively), but TAM-[Cu] at Main Creek in 2001 was disproportionately low (Fig. 4e). In both 2001 and 2004, there was no clear relationship between TAM-Cu% and WB-[Cu] in *N. acuminata* (Fig. 4g and 4h, respectively).

Although both the concentration and proportion of Zn associated with TAM (TAM-[Zn] and TAM-Zn%, respectively) were significantly correlated with the Zn whole body burden (WB-[Zn]) in *P. pugio*, both TAM-[Zn] and TAM-Zn% in *P. pugio* were generally similar among sites (40 to 60  $\mu\text{g}\cdot\text{g}^{-1}$  and ~60%, respectively) (Fig. 5a and 5b). In *N. acuminata*, TAM-[Zn] was

significantly correlated with WB-[Zn] (100 to 180  $\mu\text{g}\cdot\text{g}^{-1}$ ) (Fig. 5c), while TAM-Zn% in *N. acuminata* remained relatively constant (~60%) across the sites (Fig. 5d).

### 3.2. Metal bioaccumulation in mummichogs

In 2001, there were significant differences in whole body burdens of Cd, Pb, Cu, and Zn in mummichogs among populations (one-way ANOVA, Table 2). The whole body burdens of Cd varied from 0.03  $\mu\text{g}\cdot\text{g}^{-1}$  at Richmond Creek to 0.10  $\mu\text{g}\cdot\text{g}^{-1}$  at Great Kills Harbor (Table 2). The whole body burdens of Pb varied from ~0.25  $\mu\text{g}\cdot\text{g}^{-1}$  at Great Kills Harbor and Richmond Creek to ~0.90  $\mu\text{g}\cdot\text{g}^{-1}$  at Neck Creek, Main Creek, and Mill Creek (Table 2). The whole body burdens of Cu were similar among sites (~8  $\mu\text{g}\cdot\text{g}^{-1}$ ), except for that at Neck Creek (18.5  $\mu\text{g}\cdot\text{g}^{-1}$ ) (Table 2). The whole body burdens of Zn varied from ~140  $\mu\text{g}\cdot\text{g}^{-1}$  at Lemon Creek, Main Creek, and Richmond Creek to 193.7  $\mu\text{g}\cdot\text{g}^{-1}$  at Neck Creek (Table 2).

In 2004, there was no significant difference in whole body burdens of metals in mummichogs among populations (Cd: ~0.04  $\mu\text{g}\cdot\text{g}^{-1}$ ; Cu: ~10  $\mu\text{g}\cdot\text{g}^{-1}$ ; Zn: ~166  $\mu\text{g}\cdot\text{g}^{-1}$ , Table 2), except for Pb. The Pb whole body burden in mummichogs from Mill Creek was significantly higher (1.45  $\mu\text{g}\cdot\text{g}^{-1}$ ) than those from the other sites (~0.6  $\mu\text{g}\cdot\text{g}^{-1}$ ) (Tukey's HSD test, Table 2).

### 3.3. Relationship between TAM in prey and metal bioaccumulation in mummichogs

Significant relationships with whole body burdens of metals in mummichogs were observed only for *P. pugio* TAM-[Pb] in 2001 ( $\text{WB-[Pb]}_{\text{fish}} = 6.42 \text{ TAM-[Pb]}_{\text{prey}} + 0.11$ , Fig. 6a) and *P. pugio* TAM-[Cd] in 2004 ( $\text{WB-[Cd]}_{\text{fish}} = 0.97 \text{ TAM-[Cd]}_{\text{prey}} + 7.05$ , Fig. 6b). In both of these cases,  $\text{WB-[Pb]}_{\text{prey}}$  and  $\text{WB-[Cd]}_{\text{prey}}$  in *P. pugio* were randomly distributed without any

consistent relationship with  $WB-[Pb]_{fish}$  and  $WB-[Cd]_{fish}$  in mummichogs, respectively (Fig. 6a and 6b).

#### 4. Discussion

The relevance of metal intracellular partitioning to metal tolerance has been increasingly recognized for various marine and freshwater organisms in metal-polluted habitats (e.g., Campbell et al., 2005; Mouneyrac et al., 2003). Some experimental studies have indicated that metal detoxification strategies used by prey can influence metal trophic transfer (e.g., Rainbow et al., 2006b; Wallace et al., 1998). Despite the importance of dietary exposure to trace metals (Farang et al., 1999; Woodward et al., 1995), however, secondary implications of metal intracellular partitioning in prey to their predators (e.g., metal trophic transfer) have not been fully explored in the field setting. Although there have been many field studies on metal pollution impacts on fish (e.g., metal bioaccumulation and toxicity) in marine and freshwater ecosystems, these studies often focus on whole body burdens (e.g., Clements and Rees, 1997; Farang et al., 1999). Whole body burdens are, however, often not informative in understanding differential metal pollution impacts on fishes and shellfishes (Clements and Rees, 1997; Farang et al., 1999). Farang et al. (1999) have, for example, demonstrated that metals accumulated in macroinvertebrate prey from an intermediately polluted site in Coeur d'Alene River (Idaho, USA) were more bioavailable and subsequently caused stronger toxic effects in cutthroat trout (*Oncorhynchus clarki*) than those from a highly polluted site (Farang et al., 1999).

The results from the current study indicated that metal intracellular partitioning in an omnivorous decapod (*Palaemonetes pugio*) and a deposit-feeding polychaete (*Nereis acuminata*) in the Arthur Kill–AK were highly species- and metal- specific. For instance, although sediment-

associated cadmium (Cd) levels in the AK sites were relatively low ( $\sim 2.4$  to  $6.0 \mu\text{g}\cdot\text{g}^{-1}$ , Table 1) in 2001, a clear difference in Cd intracellular partitioning in *N. acuminata* among sites was observed. At one of the reference sites, Great Kills Harbor, nearly 80% of Cd whole body burden in polychaetes was partitioned to the trophically available metal (TAM) compartment, whereas only 30% was partitioned to TAM at one of the AK sites, Main Creek, resulting in a similar concentration of Cd associated with TAM ( $\sim 0.25 \mu\text{g}\cdot\text{g}^{-1}$ ) at these sites. In 2004, however, the proportions of TAM-Cd in *N. acuminata* in AK increased (TAM-Cd =  $\sim 45\%$ ), as the concentrations of sediment-associated Cd decreased ( $\sim 1.1$  to  $2.9 \mu\text{g}\cdot\text{g}^{-1}$ , Table 1). This differential Cd partitioning suggests that *N. acuminata* in polluted sites may sequester increasingly more Cd into insoluble granules (not part of TAM), as Cd in the environment increases. The preferential sequestration to insoluble granules has also been observed in other annelid species in chronically polluted habitats (e.g., Berthet et al., 2003; Wallace et al., 1998). The exposure-dependent 'detoxification strategy shift' to granules in benthic invertebrates appears to reflect bioavailability of sediment-bound metals (Ballan-Dufrançais et al., 2001; Berthet et al., 2003). Granules are more durable and less likely to be recycled during cellular cycling than other subcellular components such as metal-binding proteins (Rainbow et al., 2004; Wallace et al., 1998). The sequestration into granules may thus be more efficient in detoxifying metals than metal-binding proteins, allowing organisms to tolerate an elevated level of metals in the environment (Wallace et al., 1998).

Unlike *N. acuminata*, the proportions of Cd partitioned to TAM were fairly uniform ( $\sim 40\%$ ) in *P. pugio* across sites, and Cd concentration in TAM consistently increased with Cd whole body burden. This differential intracellular partitioning between *N. acuminata* and *P. pugio* may be due to the difference in feeding mode between these invertebrates (a deposit-feeder vs. an

omnivore). As a deposit-feeder, *N. acuminata* is likely to ingest a considerable amount of sediments to extract sufficient organic carbon. As a result, these polychaetes may have been exposed to more sediment-bound Cd (incidentally, whole body burdens in *N. acuminata* were more than twice as much as those in *P. pugio* at most of the study sites) and have developed higher tolerance to Cd than *P. pugio* in AK.

Despite considerable differences in Cd trophic availability from invertebrate prey among sites, Cd bioaccumulation in mummichogs varied surprisingly little. Whole body burdens of Cd in mummichogs were strongly associated with the trophically available fraction of Cd (TAM-[Cd]) only in *P. pugio* in 2004; no relationship between TAM-[Cd] in *N. acuminata* and Cd whole body burdens in mummichogs was found. In general, many fishes are known to efficiently eliminate a large amount of Cd ingested with the diet (e.g., Harrison and Curtis, 1992; Seebaugh et al., 2005). Previous feeding experiments using the reference population (Lemon Creek) have demonstrated that mummichogs are able to eliminate more than 90% of ingested Cd in *P. pugio* (Seebaugh et al., 2005). It is thus not surprising that the populations of mummichogs from chronically polluted sites can also eliminate the majority of trophically available Cd in ingested prey.

The relationship between Cd intracellular partitioning in *P. pugio* and Cd bioaccumulation in mummichogs may, however, provide some insights for differential Cd trophic availability to mummichogs in AK. For example, despite similar Cd whole body burdens in *P. pugio* from Mill Creek, Richmond Creek, and Main Creek, there was a substantial difference in TAM-Cd% among these sites (46.8, 59.1, and 73.1%, respectively). This differential Cd trophic availability from *P. pugio* among sites was clearly reflected in the Cd bioaccumulation in mummichogs at these sites. Although there have been several experimental studies on the effects of metal



detoxification in prey from chronically polluted habitats on metal trophic transfer to predators (e.g., Nott and Nicolaidou, 1994; Wallace et al., 1998), it is still unclear if detoxification strategies used by predators simultaneously influence metal trophic transfer (Goto and Wallace, 2009). Through the chronic exposure to trace metals, both prey and predators living in metal-polluted habitats may independently develop detoxification strategies, resulting in differential metal bioaccumulation in predators.

Compared to Cd, the trophic transfer efficiency for Pb is not fully explored for many organisms. Pb is often inefficiently transferred in food chains (e.g., Chen and Folt, 2000; Mikac *et al.*, 2001). However, a potential cause of low Pb trophic transfer efficiency has not been well understood. Rainbow *et al.* (2006a) have experimentally demonstrated that benthic invertebrate predators (*Nereis virens* and *Palaemonetes varians*) accumulated a considerably low amount of Pb from a deposit-feeding polychaete (*Nereis diversicolor*) collected from highly metal-polluted creeks in southwest England. The authors suggested that this low Pb trophic transfer efficiency may have been the result of its high affinity to insoluble granules (not part of TAM) in prey (Rainbow et al., 2006a). Metal-tolerant aquatic insects living in metal-polluted habitats, for example, sequester a substantial amount of Pb (more than 95% of whole body burdens) into an insoluble cellular component (Cain et al., 2000; Cain and Luoma, 1998). In the present study, similar results were also observed for both marine benthic invertebrate species (note that due to its low recovery rate, the concentration results for Pb need to be carefully considered). Although there were considerable differences in Pb whole body burdens between *P. pugio* and *N. acuminata*, in general, the proportion of Pb associated with TAM (TAM-Pb%) gradually decreased from low to high Pb-polluted sites (i.e., a reduction in Pb trophic availability to mummichogs). For example, despite its highest Pb whole body burden (in 2001), TAM-Pb% in

*N. acuminata* from Main Creek was the lowest among sites. Furthermore, despite their similar Pb whole body burdens ( $\sim 0.23 \mu\text{g}\cdot\text{g}^{-1}$ ), TAM-Pb% in *P. pugio* from Main Creek was twice as much as that in shrimp from Richmond Creek (53.7% vs. 27.2%, respectively). This differential Pb intracellular partitioning in *P. pugio* was clearly reflected in Pb bioaccumulation in mummichogs from these sites (Main Creek:  $0.94 \mu\text{g}\cdot\text{g}^{-1}$  vs. Richmond Creek:  $0.21 \mu\text{g}\cdot\text{g}^{-1}$ ). The relationships between intracellular partitioning of non-essential metals in *P. pugio* and whole body burdens in mummichogs observed in the current study may thus explain certain differential metal bioaccumulation patterns in mummichogs (i.e., prey-driven bioreduction of metals in the food chain) in AK.

Unlike Cd and Pb, intracellular partitioning of essential metals, Cu and Zn, in both invertebrate prey species varied relatively little among sites. Despite substantially elevated levels of these metals in sediments at one of the AK sites, Mill Creek (Zn: 3 to 5-fold and Cu: 4 to 16-fold more than the other sites), the variability in Cu and Zn associated with TAM in both *P. pugio* and *N. acuminata* was generally low among sites. This low variability among sites as well as relatively high TAM-Cu% and TAM-Zn% suggest that these macroinvertebrates may be able to regulate or at least tolerate these metals in AK. Similar results have also been observed in other marine and freshwater organisms (e.g., Berthet et al., 2003). Furthermore, high TAM-[Cu] in *P. pugio* observed in the current study is also likely to be associated with Cu requirement in haemocyanin by crustaceans (Rainbow, 1993; White and Rainbow, 1985).

With the exception of Cu in fish from Neck Creek in 2001, Cu and Zn bioaccumulation in mummichogs also varied little among populations ( $\sim 10 \mu\text{g Cu}\cdot\text{g}^{-1}$  and  $\sim 150 \mu\text{g Zn}\cdot\text{g}^{-1}$ , respectively). In spite of a highly elevated trophic availability (i.e., TAM-[Cu]) from *P. pugio*, the majority of ingested Cu may have been efficiently eliminated from mummichogs. Weis and

Weis (1999) have demonstrated in a field transplant experiment that, compared to crustaceans such as *P. pugio*, mummichogs accumulated substantially lower Cu after three months. In contrast, both the AK and reference populations of mummichogs accumulated a substantial amount of Zn. Compared to other metals including Cu, a large amount of Zn in mummichogs is usually deposited in calcified structures such as scales (Sauer and Watabe, 1989), suggesting that the temporary deposition of excess Zn in calcified structures may be a detoxification strategy for fish.

## 5. Conclusions

Experimental studies on metal trophic transfer are often conducted using a naïve population of predators that have not been exposed to elevated levels of trace metals in their natural habitats (e.g., Reinfelder and Fisher, 1994; Seebaugh and Wallace, 2004). As both prey and predators are chronically exposed to trace metals in metal-polluted habitats, they may independently develop differential detoxification strategies. Directly extrapolating a relationship established from laboratory experiments may thus not be applicable to metal trophic transfer and bioaccumulation in the field setting. There is an urgent need to synthesize experimental findings and field observations to understand mechanisms involved in trace metal pollution in coastal ecosystems. The results of the present study suggest that metal intracellular partitioning within prey may be partially responsible for metal trophic availability to a predator in metal-polluted habitats. However, there was also evidence that some predator-dependent processes (e.g., digestive processes) may have offset differential trophic availabilities from prey (e.g., Cd bioaccumulation in mummichogs in 2001) (Goto and Wallace, 2009). Moreover, the present study also indicated the temporal differences observed in sediment-associated metal concentrations appeared to result

in complex cascading effects on benthic invertebrates and fish (e.g., prey species-specific shifts in metal storage patterns). Further studies incorporating larger temporal as well as spatial data still need to be conducted to understand the importance of both prey- and predator- dependent processes to assess trace metal pollution in coastal ecosystems (Goto and Wallace, 2009; Rainbow et al., 2007).

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### Figure captions

Fig. 1. Map of study sites in the Arthur Kill (Mill Creek, Richmond Creek, Main Creek, and Neck Creek), New York Harbor (Great Kills Harbor) and Raritan Bay (Lemon Creek), New York.

Fig. 2. Relationships between Cd whole body burdens (WB-[Cd],  $\mu\text{g}\cdot\text{g}^{-1}$ ) and concentrations of Cd associated with TAM (TAM-[Cd],  $\mu\text{g}\cdot\text{g}^{-1}$ ) or percentages of Cd associated with TAM (TAM-Cd%) in two benthic macroinvertebrate prey species. *Palaemonetes pugio* – (a) TAM-[Cd] in 2001, (b) TAM-[Cd] in 2004, (c) TAM-Cd% in 2001, and (d) TAM-Cd% in 2004. *Nereis acuminata* – (e) TAM-[Cd] in 2001, (f) TAM-[Cd] in 2004, (g) TAM-Cd% in 2001, and (h) TAM-Cd% in 2004. Error bars indicate  $\pm 1$  SE. Solid lines indicate regression. Dashed lines indicate 95% confidence intervals.

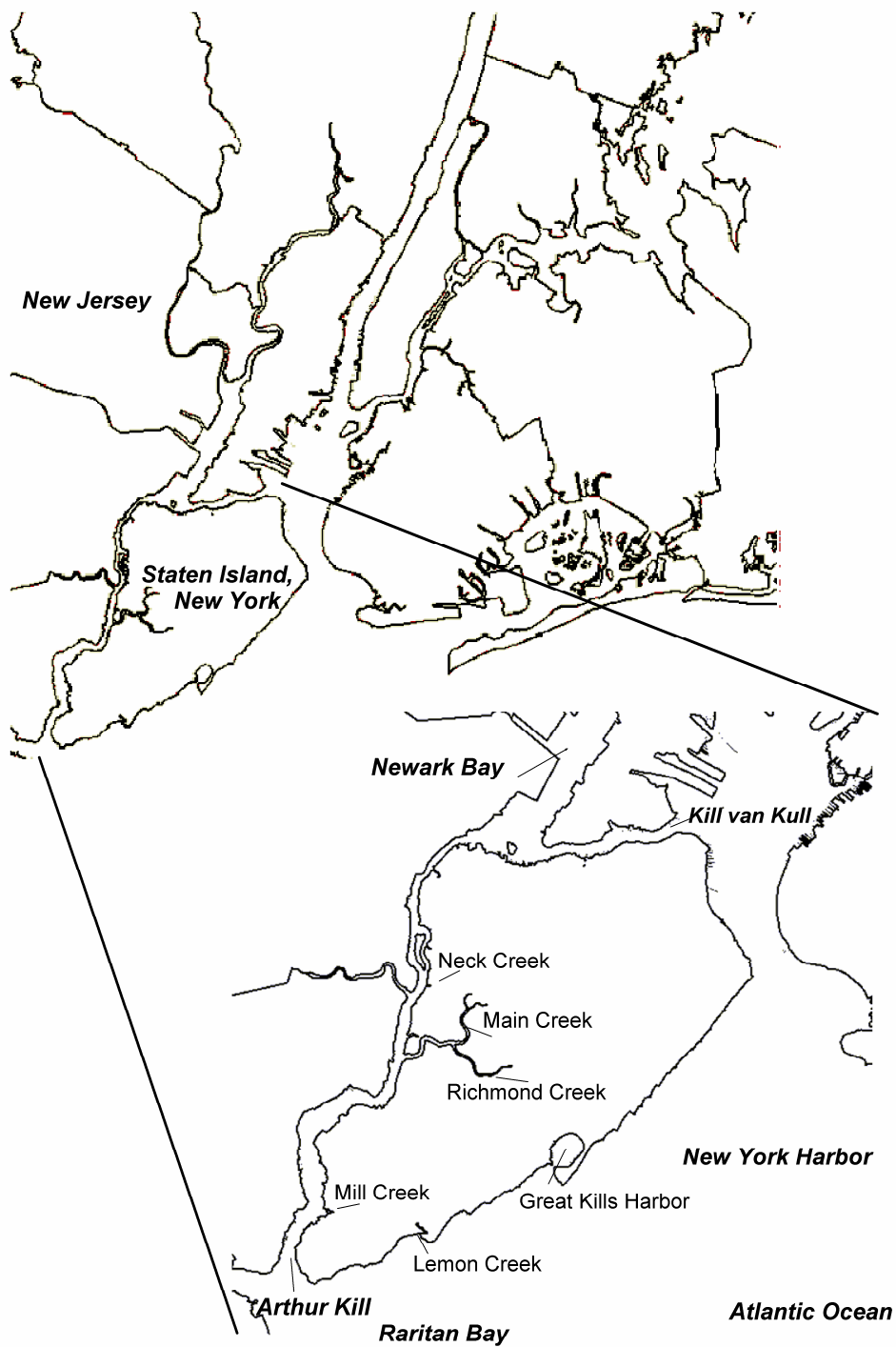


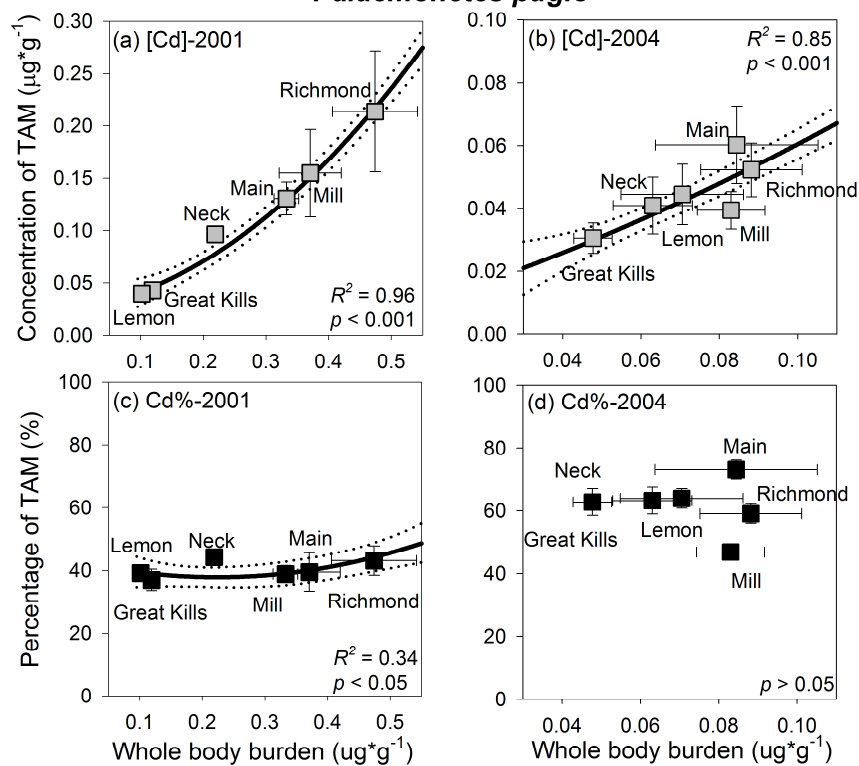
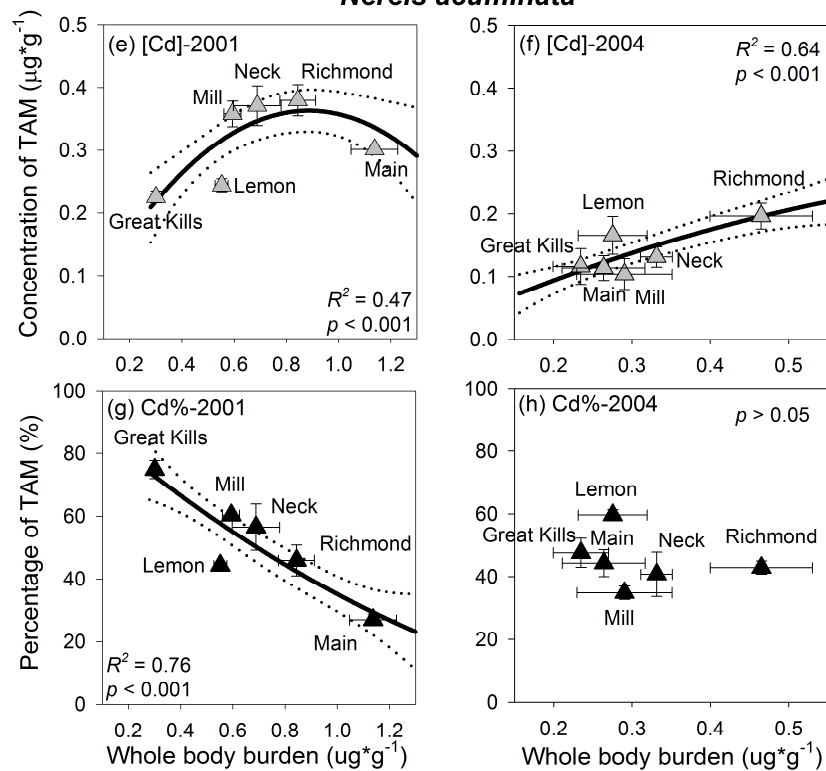
Fig. 3. Relationships between Pb whole body burdens (WB-[Pb],  $\mu\text{g}\cdot\text{g}^{-1}$ ) and concentrations of Pb associated with TAM (TAM-[Pb],  $\mu\text{g}\cdot\text{g}^{-1}$ ) or percentages of Pb associated with TAM (TAM-Pb%) in two benthic macroinvertebrate prey species. *Palaemonetes pugio* – (a) TAM-[Pb] in 2001, (b) TAM-[Pb] in 2004, (c) TAM-Pb% in 2001, and (d) TAM-Pb% in 2004. *Nereis acuminata* – (e) TAM-[Pb] in 2001, (f) TAM-[Pb] in 2004, (g) TAM-Pb% in 2001, and (h) TAM-Pb% in 2004. Error bars indicate  $\pm 1$  SE. Solid lines indicate regression. Dashed lines indicate 95% confidence intervals.

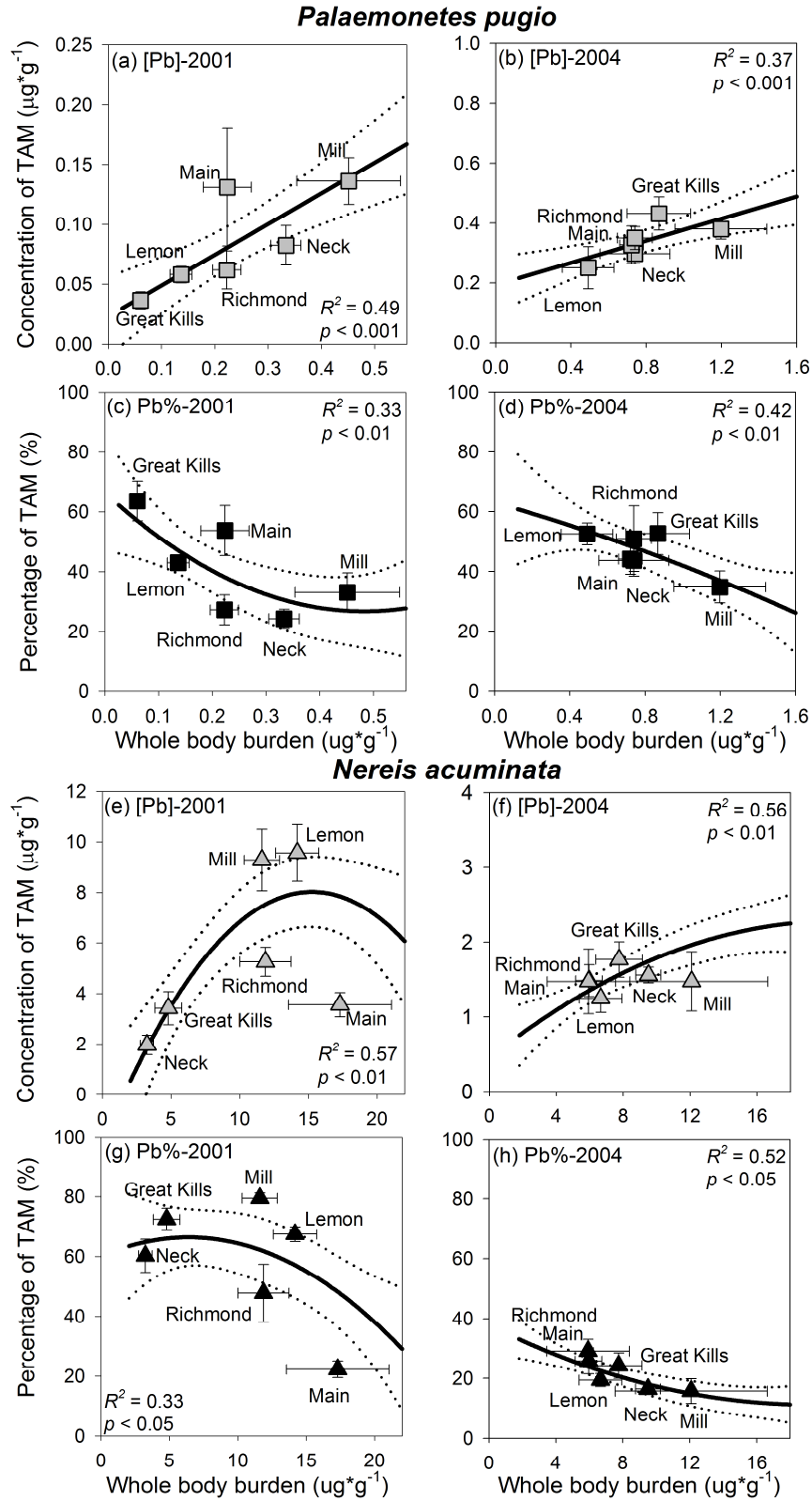
Fig. 4. Relationships between Cu whole body burdens (WB-[Cu],  $\mu\text{g}\cdot\text{g}^{-1}$ ) and concentrations of Cu associated with TAM (TAM-[Cu],  $\mu\text{g}\cdot\text{g}^{-1}$ ) or percentages of Cu associated with TAM (TAM-Cu%) in two benthic macroinvertebrate prey species *Palaemonetes pugio* – (a) TAM-[Cu] in 2001, (b) TAM-[Cu] in 2004, (c) TAM-Cu% in 2001, and (d) TAM-Cu% in 2004. *Nereis acuminata* – (e) TAM-[Cu] in 2001, (f) TAM-[Cu] in 2004, (g) TAM-Cu% in 2001, and (h) TAM-Cu% in 2004. Error bars indicate  $\pm 1$  SE. Solid lines indicate regression. Dashed lines indicate 95% confidence intervals.

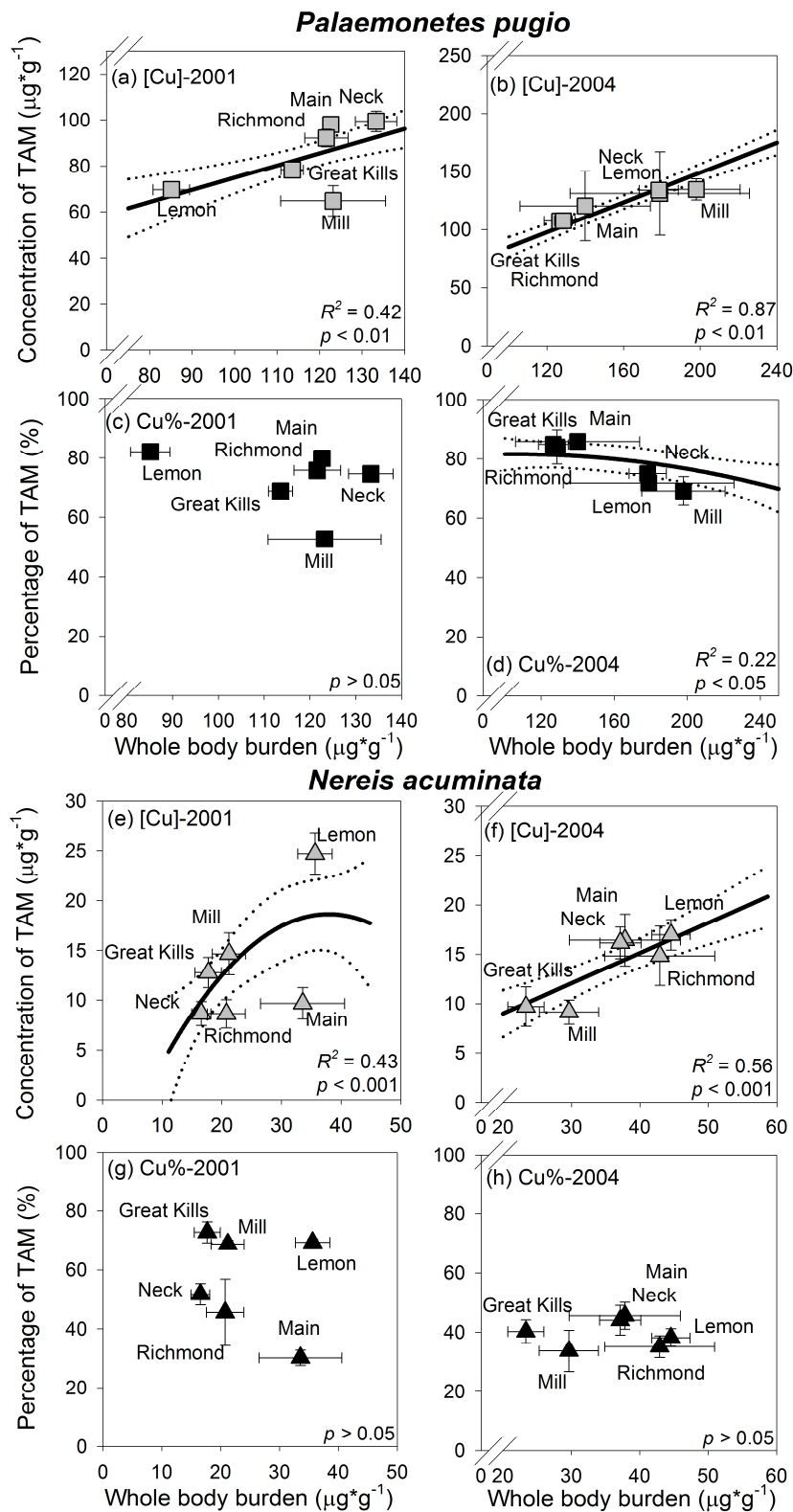
Fig. 5. Relationships between Zn whole body burdens (WB-[Zn],  $\mu\text{g}\cdot\text{g}^{-1}$ ) and concentrations of Zn associated with TAM (TAM-[Zn],  $\mu\text{g}\cdot\text{g}^{-1}$ ) or percentages of Zn associated with TAM (TAM-Zn%) in two benthic macroinvertebrate prey species in 2001. *Palaemonetes pugio* – (a) TAM-[Zn] and (b) TAM-Zn%. *Nereis acuminata* – (c) TAM-[Zn] and (d) TAM-Zn%. Error bars indicate  $\pm 1$  SE. Solid lines indicate regression. Dashed lines indicate 95% confidence intervals. Samples for 2004 were not available.

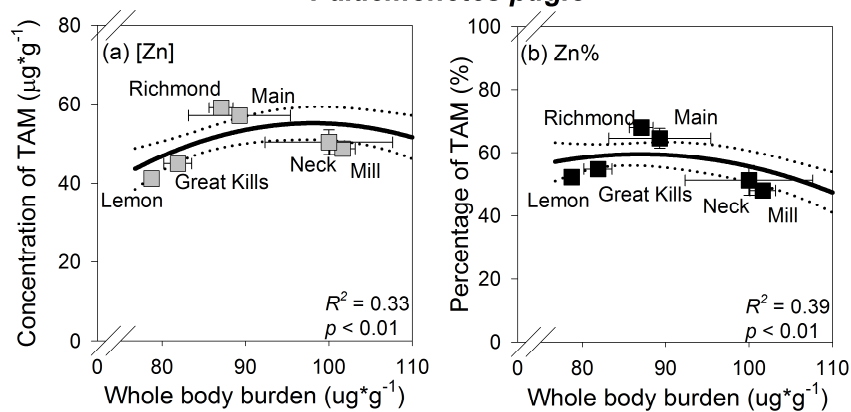
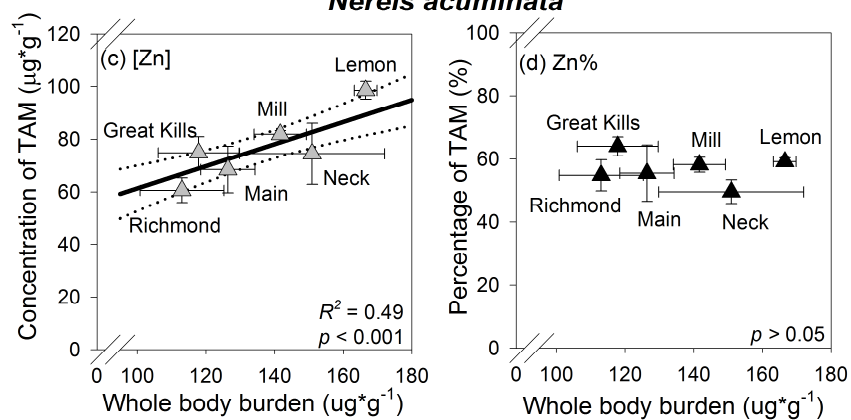
Fig. 6. (a) Relationships between Pb whole body burdens (WB-[Pb]<sub>fish</sub>,  $\mu\text{g}\cdot\text{g}^{-1}$ ) in mummichogs and concentrations of Pb associated with TAM (TAM-[Pb]<sub>prey</sub>,  $\mu\text{g}\cdot\text{g}^{-1}$ ) ( $\blacktriangledown$ ) or Pb whole body burdens (WB-[Pb]<sub>prey</sub>,  $\mu\text{g}\cdot\text{g}^{-1}$ ) in *Palaemonetes pugio* ( $\bullet$ ) in 2001; and (b) Relationships between Cd whole body burdens (WB-[Cd]<sub>fish</sub>,  $\mu\text{g}\cdot\text{g}^{-1}$ ) in mummichogs and concentrations of Cd associated with TAM (TAM-[Cd]<sub>prey</sub>,  $\mu\text{g}\cdot\text{g}^{-1}$ ) ( $\blacktriangledown$ ) or Cd whole body burdens (WB-[Cd]<sub>prey</sub>,  $\mu\text{g}\cdot\text{g}^{-1}$ ) in *Palaemonetes pugio* ( $\bullet$ ) in 2004. The solid lines indicate the least squares regression between (a) TAM-[Pb]<sub>prey</sub> and WB-[Pb]<sub>fish</sub>, or (b) TAM-[Cd]<sub>prey</sub> and WB-[Cd]<sub>fish</sub>.



*Palaemonetes pugio**Nereis acuminata*





*Palaemonetes pugio**Nereis acuminata*

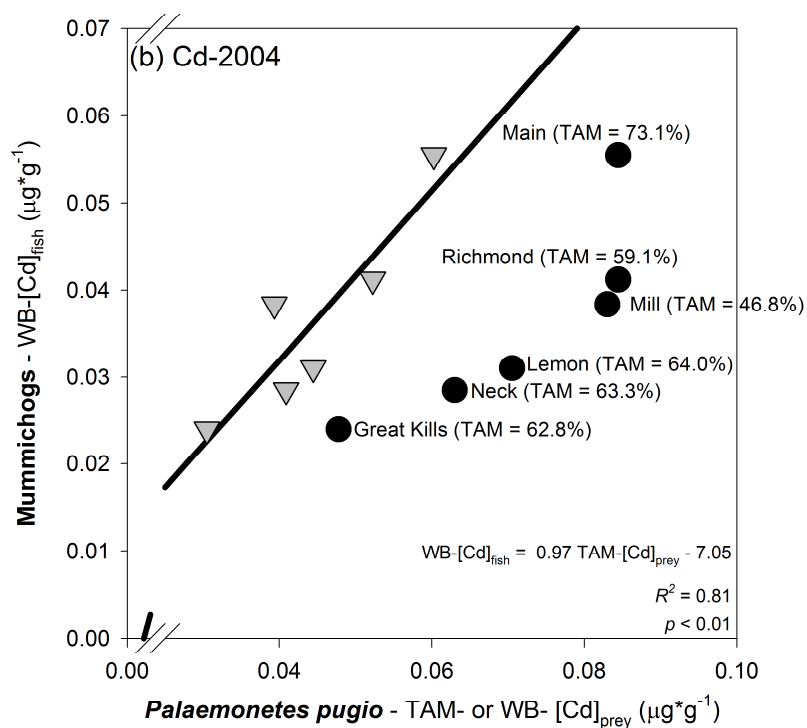
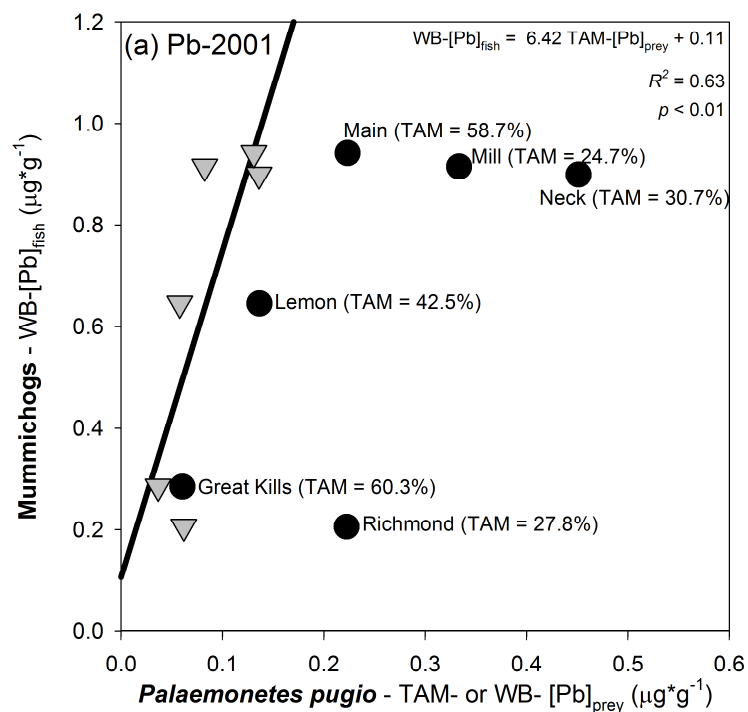


Table 1  
 Mean concentrations of metals ( $\mu\text{g}\cdot\text{g}^{-1}$ ) in sediments collected from the study sites in 2001 and 2004<sup>†</sup>

Trace metals ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Study sites											
	Lemon Creek		Great Kills Harbor*		Mill Creek		Richmond Creek		Main Creek		Neck Creek	
	2001	2004	2001	2004	2001	2004	2001	2004	2001	2004	2001	2004
Cd	2.4	1.2	–	1.1	6.0	2.9	5.7	1.6	5.2	2.9	2.8	1.1
Cu	91.3	124.8	–	92.2	1483.5	911.5	266.9	99.7	294.4	216.5	238.8	152.5
Pb	27.5	83.9	–	98.7	402.8	655.5	63.8	91.9	58.0	171.3	80.4	214.7
Zn	107.8	220.5	–	188.4	555.9	1193.3	293.0	289.0	336.7	410.9	165.8	339.0

<sup>†</sup>Sources of the data: Ward (2002) for 2001 and Goto (2009) for 2004.

\*Sediment samples from Great Kills Harbor were not available in 2001.



Table 2

Mean whole body burdens of Cd, Pb, Cu, and Zn ( $\mu\text{g}\cdot\text{g}^{-1}$ ) in mummichogs collected from the study sites in 2001 and 2004

Study sites	2001	Cd	Pb	Cu	Zn	2004	Cd	Pb	Cu	Zn
Lemon Creek		0.06 <sub>B</sub>	0.65 <sub>AB</sub>	6.98 <sub>A</sub>	138.16 <sub>B</sub>		0.03	0.66 <sub>A</sub>	16.10	146.77
Great Kills Harbor		0.10 <sub>A</sub>	0.28 <sub>A</sub>	7.48 <sub>A</sub>	158.12 <sub>AB</sub>		0.02	0.60 <sub>A</sub>	8.37	173.95
Mill Creek		0.08 <sub>AC</sub>	0.90 <sub>B</sub>	10.66 <sub>A</sub>	161.67 <sub>AB</sub>		0.05	1.45 <sub>B</sub>	10.74	182.47
Richmond Creek		0.03 <sub>D</sub>	0.21 <sub>A</sub>	7.11 <sub>A</sub>	143.56 <sub>B</sub>		0.04	0.58 <sub>A</sub>	9.88	178.01
Main Creek		0.09 <sub>AC</sub>	0.94 <sub>B</sub>	7.75 <sub>A</sub>	143.93 <sub>B</sub>		0.03	0.62 <sub>A</sub>	8.96	124.02
Neck Creek		0.06 <sub>BC</sub>	0.92 <sub>B</sub>	18.50 <sub>B</sub>	193.70 <sub>A</sub>		0.02	0.60 <sub>A</sub>	11.53	153.97

Different letters indicate statistically significant difference among sites (one-way ANOVA followed by Tukey's HSD test,  $p < 0.05$ ).